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Calculation of Rate Coefficients for some Elementary Reactions

1. Hydrogen, Deuterium, and Deuterium Hydride with Chlorine

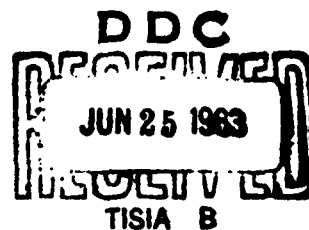
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Prepared by ROGER L. WILKINS
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Prepared for COMMANDER SPACE SYSTEMS DIVISION

UNITED STATES AIR FORCE

Inglewood, California



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CALCULATION OF RATE COEFFICIENTS FOR SOME ELEMENTARY REACTIONS

I. Hydrogen, Deuterium, and Deuterium Hydride with Chlorine

Roger L. Wilkins
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ABSTRACT

Rate coefficients ~~are~~ calculated for the reactions of hydrogen, deuterium, and deuterium hydride with chlorine. The potential energy surfaces of the isotopic transition complexes of HCl_2 and H_2Cl ~~have been~~ constructed by the Sato method to match experimental activation energies in accordance with absolute rate theory. The rate coefficients calculated using absolute rate theory are then used to evaluate the relative rates of reaction of H_2/HD , H_2/D_2 with chlorine atoms, and the relative rates of the fast reaction step $\text{H} + \text{Cl}_2$ compared to the back reaction $\text{H} + \text{HCl}$. The results agree very well with the few experimental values reported in the literature. ~~Our~~ theoretical calculations show that prior experimental values of the pre-exponential factors in the Arrhenius-type expression for rate constants are not required in order to obtain better information on the structure and vibrational frequencies of the transition states. ~~The~~ agreement of the activated complex theory with experiment was ~~found to be~~ satisfactory.

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CALCULATION OF RATE COEFFICIENTS FOR SOME ELEMENTARY REACTIONS

I. Hydrogen, Deuterium, and Deuterium Hydride with Chlorine

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INTRODUCTION

Jones¹ measured the relative rates of reaction of H_2 and HT with chlorine atoms, and Ashmore and Chanmugan² measured the slow reaction between hydrogen molecules and chlorine atoms. Measurements have been made of the relative rates of reaction of chlorine atoms with H_2 and D_2 by Rollefson³, with mixtures of H_2 , HD, and D_2 by Bigeleisen, et al.⁴ and Farkas⁵ and of Cl_2 with H, and H with HCl .⁶ In Fig. 1 some of these experimental data are compared with values calculated by Wheeler, Topley, and Eyring⁷ using the London potential. The value of the largest discrepancy in the ratio of the experimental relative rates to these theoretical relative rates is about five. In addition, the difference in theoretical activation energies for the reactions of H_2 with Cl, and HT with Cl, has the opposite sign from that of the experimental data.

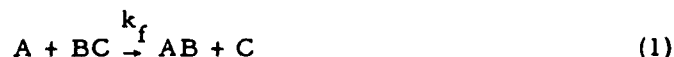
Bigeleisen and Wolfsberg⁸ obtained satisfactory agreement between theory and experiment by using the experimental value of the pre-exponential factor for the relative rates of reaction of mixtures of H_2 , HD, and D_2 with Cl to estimate the symmetrical stretching vibration in the H_2Cl transition state. More recently, Klein and Wolfsberg⁶ have used a similar procedure

to estimate the doubly degenerate bending vibration in the HCl_2 transition state. These estimated frequencies are based on low temperature measurements.

In this study, the fundamental vibrations of each activated complex are calculated without prior information on the experimental values of the pre-exponential factors. The molecular data for the activated complex obtained from the potential energy surfaces using the Sato method⁹, along with molecular structure data for the reactants, are used to calculate the absolute reaction rates of hydrogen, deuterium, and deuterium hydride with chlorine. The theoretical results are compared with experimental values for the relative rates of reaction of H_2/HD , H_2/D_2 with chlorine atoms, and for the rate of the fast reaction step $\text{H} + \text{Cl}_2$ relative to that of the back reaction $\text{H} + \text{HCl}$.

COMPUTATIONAL PROCEDURE

Consider the elementary exchange reaction



The theory of absolute rates¹⁰ gives the following formula for the rate coefficient k_f of this elementary exchange reaction:

$$k_f = \kappa \tau \left(\frac{kT}{h} \right) \frac{Q_c}{Q_a Q_m} \exp(-E_0/kT) \quad (2)$$

In Eq. (2) the subscripts c, a, and m refer to the activated complex, the reactant atom, and the reactant molecule, respectively; κ is the transmission coefficient, Q is the total partition function, τ is the tunnel effect correction factor, E_0 is the classical activation energy with zero-level correction, and the other symbols have common meanings. Substitution of the proper

partition functions¹¹ for both complex and reactants allows one to write Eq. (2) as

$$k_f = A(T)\exp[-E_0/(kT)] \quad (3)$$

where the pre-exponential factor

$$A(T) = \kappa \tau \left(\frac{m_c}{m_m m_a} \right)^{3/2} \left(\frac{I_c}{I_m} \right) \left(\frac{\sigma_m}{\sigma_c} \right) \frac{1}{T^{3/2}} (1 - \exp[-(h\nu)/(kT)]) \prod_{j=1}^3 (1 - \exp[-(h\nu_j)/(kT)]) \quad (4)$$

and m is the mass, I is the moment of inertia, σ is the symmetry number, ν is the vibrational frequency of the diatomic molecule, and ν_j is the frequency of the complex. The moment of inertia of the complex and the vibrational frequencies of the complex are calculated from the potential energy surface constructed to interpret the chemical reaction. One must assume a priori some structure for the transition complex before the potential energy surface can be constructed. For the computations made in this study, a linear structure is assumed for the activated complex since the smallest increase in the potential energy of the system results if all three atoms remain on a straight line. The vibrational frequencies of the transition complex are obtained from the force constants of the energy surface by the method of small vibration analysis. For a linear transition state complex consisting of three atoms, there are one symmetric stretching frequency ν_s , one bending frequency ν_b which is doubly degenerate, and an imaginary asymmetric stretch frequency ν_u . The imaginary vibrational frequency ν_u affects the reaction rate only through the tunnelling correction factor τ . The tunnelling correction is quite large at room temperature but is less significant at temperatures in excess of 500°K.

Recently, Sato⁹ proposed a new method for drawing the potential energy surface required to interpret chemical reactions. This method is not an absolute one, since one parameter K (the square of the overlap integral) is an adjustable parameter. The Sato potential gives results slightly different from the London potential¹² used by Eyring and Polanyi. The essential differences between the Sato method and the Eyring method of constructing potential energy surfaces have been discussed adequately in a recent paper by Weston¹³.

An electronic computer was used to calculate the potential energy surface of a system of three atoms using the Sato method of constructing potential energy surfaces. In a system consisting of three atoms, if one atom is kept at infinite separation from the other two, then two equations for the energy of the bonding and antibonding states derived by the Heitler-London method are:

(for bonding states)

$$E_{ij}^b = (Q_{ij} + a_{ij}) / (1 + S_{ij}^2) = (Q_{ij} + a_{ij}) / (1 + K) \quad (5)$$

(for antibonding states)

$$E_{ij}^a = (Q_{ij} - a_{ij}) / (1 - S_{ij}^2) = (Q_{ij} - a_{ij}) / (1 - K) \quad (6)$$

In these equations Q_{ij} is the Coulomb energy for atoms i and j, a_{ij} and S_{ij} are the corresponding exchange integral and overlap integral, respectively, and K is the square of the overlap integral. The energy for the bonding state was calculated by using the More potential function

$$E_{ij}^b = D_{ij} \left[\exp[-2\beta_{ij}(r_{ij} - r_{ij}^0)] - 2 \exp[-\beta_{ij}(r_{ij} - r_{ij}^0)] \right] \quad (7)$$

where D_{ij} is the dissociation energy, r_{ij} is the distance between atoms i and j , r_{ij}^0 is this distance in the equilibrium configuration, and β_{ij} is a constant obtained from spectroscopic data. For the energy of the antibonding states, Sato proposed:

$$E_{ij}^a = \frac{D_{ij}}{2} \left[\exp[-2\beta_{ij}(r_{ij} - r_{ij}^0)] + 2 \exp[-\beta_{ij}(r_{ij} - r_{ij}^0)] \right] \quad (8)$$

This relationship for the energy of an antibonding state agrees well with the calculated data for the energy of the repulsive state of hydrogen obtained by more exact methods^{14, 15}. If one assumes K is a constant for a specified system, then Eqs. (5)-(8) can be solved for Q_{ij} and a_{ij} as a function of r_{ij} . The total energy for each configuration is obtained from the London¹² equation for a system of three atoms

$$E = (1 + K)^{-1} \left\{ Q_{12} + Q_{13} + Q_{23} \pm \left[\frac{1}{2}(a_{12} - a_{13})^2 + \frac{1}{2}(a_{12} - a_{23})^2 + \frac{1}{2}(a_{13} - a_{23})^2 \right]^{\frac{1}{2}} \right\} \quad (9)$$

The saddle point locus and three force constants f_1 , f_2 , and f_{12} corresponding to the activated complex were evaluated by the method of least squares. The bending force constant f_ϕ by definition is

$$f_\phi = \left(\frac{\partial^2 E}{\partial \phi^2} \right)_{r_{12}, r_{23}} \quad (10)$$

Since r_{13} and ϕ are related by the cosine law, it is easy to show that the bending force constant for a linear complex is:

$$\frac{f_{\phi}}{r_{12}r_{23}} = - \frac{1}{r_{13}} \left(\frac{\partial E}{\partial \phi^2} \right)_{r_{12}, r_{23}} \quad (11)$$

and by use of Eq. (9)

$$\left(\frac{\partial E}{\partial r_{13}} \right)_{r_{12}, r_{23}} = (1 + K)^{-1} \left\{ \left(\frac{\partial Q_{13}}{\partial r_{13}} \right)_{r_{12}, r_{23}} - \frac{\left[a_{13} - \frac{1}{2}(a_{12} + a_{23}) \left(\frac{\partial a_{13}}{\partial r_{13}} \right)_{r_{12}, r_{23}} \right]}{\sqrt{\frac{1}{2}(a_{12} - a_{13})^2 + \frac{1}{2}(a_{12} - a_{23})^2 + \frac{1}{2}(a_{13} - a_{23})^2}} \right\} \quad (12)$$

By the method of small vibrations¹⁶, the frequencies for a transition state composed of three atoms become:

$$\nu_s = \frac{\sqrt{N}}{2\pi c} \left\{ \frac{a + \left[a^2 - 4M_1M_2M_3M(f_1f_2 - f_{12}) \right]^{\frac{1}{2}}}{2M_1M_2M_3} \right\}^{\frac{1}{2}} \quad (13)$$

$$\nu_b = \frac{\sqrt{N}}{2\pi c} \left[\left(\frac{f_{\phi}}{r_{12}r_{23}} \right) \frac{1}{r_{12}r_{23}} MI / M_1M_2M_3 \right]^{\frac{1}{2}} \quad (14)$$

$$\nu_u = \frac{\sqrt{N}}{2\pi c} \left\{ \frac{a - \left[a^2 - 4M_1M_2M_3M(f_1f_2 - f_{12}) \right]^{\frac{1}{2}}}{2M_1M_2M_3} \right\}^{\frac{1}{2}} \quad (15)$$

where

$$a = M_1(M_2 + M_3)f_1 + M_3(M_2 + M_1)f_2 - 2M_1M_3f_{12}$$

The moments of inertia of the complex and for the molecule are given by

$$I_c = \frac{1}{M} \left[M_1(M_2 + M_3)r_{12}^2 + 2M_1M_2r_{12}r_{23} + M_3(M_1 + M_2)r_{23}^2 \right] \quad (16)$$

$$I_m = \frac{M_2M_3}{M_2 + M_3} (r_{23}^0)^2 \quad (17)$$

In one dimension, the energy surface of the reaction path has a negative curvature corresponding to a maximum potential energy. For reactions involving light particles, penetration through the energy barrier is significant below 500°K. The quantum correction for penetration of such particles through the energy barrier is called the tunnel effect. Using the WBK approximation, Bell¹⁷ has recently obtained the permeability $G(W)$ of a parabolic potential barrier as a function of the energy W of the incident particle of mass m :

$$G(W) = [1 + \exp(\beta y)]^{-1} \quad (18)$$

where

$$y = 1 - \frac{W}{E}$$

$$\beta = 2\pi^2 a(2mE)^{1/2}/h$$

and E and $2a$ are the height and width of the barrier. The quantum correction for the reaction velocity is obtained by averaging the permeability $G(W)$ over Maxwell-Boltzmann energy distribution

$$\begin{aligned} \tau &= \frac{1}{RT} \exp(E/RT) \int_0^\infty \exp(-W/RT) G(W) dW \\ &= \frac{\pi a/\beta}{\sin \pi a/\beta} - \frac{a \exp(a-\beta)}{\beta-a} \left[1 + \sum_{n=1}^{\infty} (-1)^n \frac{\beta-a}{(n+1)\beta-a} \exp(-n\beta) \right] \end{aligned} \quad (19)$$

where $a = E/kT$.

The permeability $G(W)$ is a poor approximation when $W \sim E$ because the WBK approximation is valid only when $W \ll E$. This approximation is therefore valid only when the degree of tunnelling is large. The assumption that $G(W) = 1$ for $W > E$ neglects the reflection of particles which takes place when the value of $W \sim E$.

If one writes

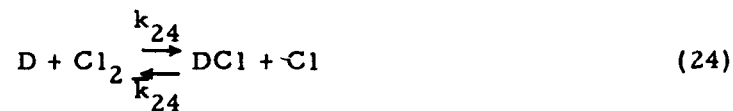
$$u = 2\pi a/\beta = -ih\nu_u/kT \quad (20)$$

then the Bell solution for the tunnelling correction effect reduces to the Wigner $u^2/24$ correction for small tunnelling. The tunnelling correction factor is evaluated by calculating the value of E corresponding to the best parabolic fit to the Sato energy barrier over which there is appreciable tunnelling. This procedure is a better approximation to the parabolic barrier than is the parabolic fit obtained from the harmonic frequency corresponding to the curvature at the top of the potential energy barrier. At temperatures below 500°K , this tunnelling correction is usually very large and most calculations indicate that the potential barrier calculated by the Sato method is too narrow. With such large values of the tunnel correction, one finds a

non-Arrhenius dependence in both the absolute and relative rates. This does not agree with the experimental facts. Subsequently, we calculated rate constants which included the tunnel effect at temperatures above 500°K and extrapolated for the values of the rate constants below 500°K.

RESULTS AND DISCUSSION

The following elementary reactions can occur between chlorine and a mixture of H₂, HD, and D₂:



The isotopic competitive method¹⁹ is usually used to measure the relative rates of isotopic reactions. In the case of reactions (21) and (22) it is very difficult to reproduce the chain length experimentally. Unless reaction (22) can be quenched, an experiment designed to measure the relative rates of reaction of H₂/HD with Cl atoms will in reality measure $R = k_{21}/(k_{25} + k_{26})$. Although measurements of the individual ratios k_{21}/k_{25} and k_{21}/k_{26} would be preferable, this is difficult. However, Bigeleisen, et al⁴, evaluated the relative rate R by intercomparing the isotopic composition of the unreacted hydrogen at measured amounts of reaction. A correction was made by Bigeleisen, et al, for the presence of D₂ which could be formed by the backward reactions (23) and (24).

Portions of the Sato potential energy surfaces for reactions (21)-(26) are shown in Figs. 2-7. These potential surfaces are for linear configurations A-B-C with r_{12} , r_{23} as the coordinates between atoms A and B, and B and C, respectively. In these plots the contour lines are expressed in units of kcal/mole. The experimental activation energy of reactions (21) and (22) were used to determine the parameter K. The same value of K was used for isotopic modifications of reactions (21) and (22).

The pre-exponential factors for reactions (21)-(26) were calculated by the procedure described under COMPUTATIONAL PROCEDURE with the parameters of the reactants in Table I and those of the linear activated complexes in Tables II and III. The anharmonicity corrections to the real frequencies were neglected since Weston¹³ showed that this effect is negligible for the H₃ transition state when compared to other uncertainties of the Sato method. The tunnelling correction τ was calculated from the expression obtained by Bell (Eq. 19). The harmonic force constant which corresponds to the imaginary frequency of the reaction coordinate was not used to evaluate the tunnelling correction factor for each reaction. Instead, a new imaginary frequency was calculated for each reaction by fitting the best obtainable parabolic potential to the Sato barrier over that region where tunnelling is appreciable. The transmission coefficient of one-half was used for isotopically mixed molecules, and of unity for all others.

Figure 8 compares the $\log k_{21}$ obtained experimentally with that calculated in this paper. The theoretical absolute rates for k_{21} calculated from the Sato potential agree quite well with that of the experimental data. The experimental value of k_{21} obtained by Ashmore and Chanmugam² at 523°K compares favorably with the results of Rideal and Steiner²⁰ at 1000°K and of Klingelhoefer and Rodebush²¹ at room temperature. These three experimental points lie on a straight line; from the slope of this line the activation energy of reaction (21) is 5.500 ± 0.200 kcal/mole. This value of the activation energy compares favorably with a value of 5.90 kcal/mole calculated by Rideal and Steiner from their experimental data at 1000°K and 5.6 kcal/mole, which they calculated from the results of Klingelhoefer and Rodebush.

The relative rates of reactions of



and



were determined in the temperature range 273-335°K by Klein and Wolfsberg⁶. They found that the relative rate is

$$\frac{\bar{k}_{21}}{k_{22}} = (0.143 \pm 0.033) \exp -(1540 \pm 130/RT) \quad (27)$$

Klein and Wolfsberg used the pre-exponential factor in Eq. (27) to determine the doubly degenerate bending frequency of the linear transition state HCl_2 , and found it to have a value of about $105 \pm 20 \text{ cm}^{-1}$. We evaluated the doubly

degenerate bending frequency for a linear transition state HCl_2 from the force constants (Table III), and found it to be 51 cm^{-1} . The Klein and Wolfsberg calculation assumes that the stretching frequency of the HCl_2 transition state is large enough to be neglected in the temperature range of their study and that this frequency will be larger than the Cl_2 frequency. The latter conclusion was based on their findings with respect to the H_2Cl transition state, where the most reasonable model for the H_2Cl transition state was one with a large H-Cl force constant. Our calculation (Table III) shows that the stretching frequency of the HCl_2 transition state is lower than the Cl_2 frequency. In addition, we calculated the H-Cl and Cl-Cl distances in the HCl_2 transition state to be $r_{\text{H-Cl}} = 2.005\text{\AA}$ and $r_{\text{Cl-Cl}} = 2.252\text{\AA}$. Klein and Wolfsberg estimated $r_{\text{H-Cl}} = 1.5\text{\AA}$ and $r_{\text{Cl-Cl}} = 2.2\text{\AA}$. Consequently we re-evaluated the bending frequency of the HCl_2 transition states, using the data in Tables I-III for the HCl_2 and H_2Cl transition states along with the experimental value of the pre-exponential factor obtained by Klein and Wolfsberg (Eq. 27). The doubly degenerate bending frequency was found to be $68 \pm 20 \text{ cm}^{-1}$, which agrees better with the value obtained from the force constants calculated from the Sato potential barrier for the HCl_2 linear transition state. A comparison of the relative rates of reaction (21) and (22) is shown in Fig. 9. The theoretical absolute relative rates of reaction of \bar{k}_{21}/k_{22} calculated from the Sato potential agree with the experimental data within 20 percent.

Figure 10 contains a plot of the relative rates of reaction of H_2 and HD with chlorine atoms. Bigeleisen, et al⁴, measured these rates over the temperature range $243\text{--}350^\circ\text{K}$ and found that

$$R = \frac{k_{21}}{k_{25} + k_{26}} = (1.24 \pm 0.03) \exp(490 \pm 6/RT) \quad (28)$$

It can be seen from Fig. 10 that our calculated values of R agree very well with experimental values.

A plot of the relative rates of reaction of H_2 and D_2 with chlorine atom based on the parameters given in Tables I-III is given in Fig. 11. We note that $\log k_{21}/k_{23}$ is larger than the experimental values. Bigeleisen, et al, suggested that their calculated values of $\log k_{21}/k_{23}$ could be brought into closer agreement with the experimental values by choosing the bending frequency of the H_2Cl complex larger than 200 cm^{-1} and the imaginary frequency smaller than $720i$. Since in this study no attempts were made to fit the theoretical structure of the complex to the experimental data, it is interesting to note that even here the theoretical values are within a factor of three of the only two experimental points reported by Rollefson³. Our calculated difference in energies $E_{23}-E_{21}$ of 1.17 kcal/mole compares favorably with Rollefson's $E_{23}-E_{21}$ of 1.63 kcal/mole. Rollefson states that a 10-percent error in one of the two measurements of the ratio k_{21}/k_{23} corresponds to a change of 0.54 kcal/mole in $E_{23}-E_{21}$ and a change in the relative rates of a factor of 2.7. The latter would suggest that additional experiments should be carried out before absolute rate theory can be used to test the relative rates of reactions (21) and (23).

CONCLUSION

These theoretical calculations show that the rates obtained from absolute reaction rate theory with a Sato potential energy function agree very well with the few experimental values reported in the literature. Indeed, they show that the experimental values of the pre-exponential factors in the Arrhenius-type expression for rate constants are not required to obtain better information on the structure and vibrational frequencies of the transition states. The agreement between theory and experiment constitutes a positive test of the usefulness of this transition-state formulation in the evaluation of absolute reaction rates.

Table I. Properties of Reactants

| Substance | $r_0(\text{\AA})$ | $\omega_e(\text{cm}^{-1})$ | $\omega_e x_e(\text{cm}^{-1})$ | $D_e^0(\text{kcal/mole})$ |
|-----------------|-------------------|----------------------------|--------------------------------|---------------------------|
| H ₂ | 0.74166 | 4395.24 | 117.995 | 109.18 |
| HCl | 1.27460 | 2989.74 | 52.05 | 106.31 |
| Cl ₂ | 1.988 | 564.9 | 4. | 57.876 |
| D ₂ | 0.74164 | 3118.46 | 64.097 | 109.296 |
| DH | 0.74130 | 3817.09 | 94.958 | 109.228 |
| DC1 | 1.27490 | 2090.78 | 29.40 | 106.335 |

Table II. Parameters of Linear Activated Complexes

| Complex | $r_{12}(A)$ | $r_{23}(A)$ | $I(\text{gm cm}^2) \times 10^{39}$ | Force Constants * | | | |
|-------------------------------|-------------|-------------|------------------------------------|-------------------|-------|----------|-----------------------|
| | | | | f_1 | f_2 | f_{12} | $f_\phi/r_{12}r_{23}$ |
| HC1C1 | 2.005 | 2.252 | 16.544 | 2.890 | .125 | .209 | 0.00121 |
| HHC1 | 1.420 | 0.970 | 1.062 | 1.443 | .593 | 1.549 | 0.02236 |
| DC1C1 | 2.005 | 2.273 | 18.412 | 2.878 | .120 | .208 | 0.00131 |
| DHC1 | 1.424 | 0.968 | 1.926 | 1.378 | .580 | 1.576 | 0.02268 |
| HDC1 | 1.421 | 0.973 | 1.193 | 1.422 | .565 | 1.510 | 0.02208 |
| DDC1 | 1.424 | 0.972 | 2.046 | 1.375 | .468 | 1.497 | 0.02244 |
| * In units of 10^5 dynes/cm | | | | | | | |

Table III. Fundamental Frequencies and Activation Energies of Linear Activated Complexes

| Reaction | $\omega_1(\text{cm}^{-1})$ | $\omega_2(\text{cm}^{-1})$ | $\omega_3(\text{cm}^{-1})$ | $\omega_3(\text{cm}^{-1})^*$ | K | $E_c(\text{kcal/mole})$ | $E_0(\text{kcal/mole})$ |
|---|----------------------------|----------------------------|----------------------------|------------------------------|-------|-------------------------|-------------------------|
| $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ | 514 | 51 | 473i | 555i | 0 | 2.42 | 2.493 |
| $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ | 1095 | 428 | 1385i | 980i | 0.168 | 5.63 | 4.14 |
| $\text{D} + \text{Cl}_2 \rightarrow \text{DCl} + \text{Cl}$ | 509 | 40 | 332i | 346i | 0 | 2.45 | 2.48 |
| $\text{D} + \text{HCl} \rightarrow \text{DH} + \text{Cl}$ | 329 | 416 | 1250i | 785i | 0.168 | 6.19 | 3.47 |
| $\text{H} + \text{DCl} \rightarrow \text{HD} + \text{Cl}$ | 1088 | 323 | 1017i | 960i | 0.168 | 5.57 | 5.06 |
| $\text{D} + \text{DCl} \rightarrow \text{D}_2 + \text{Cl}$ | 641 | 305 | 959i | 700i | 0.168 | 5.92 | 4.72 |
| * Value of ω_3 which best fits Sato potential barrier. | | | | | | | |

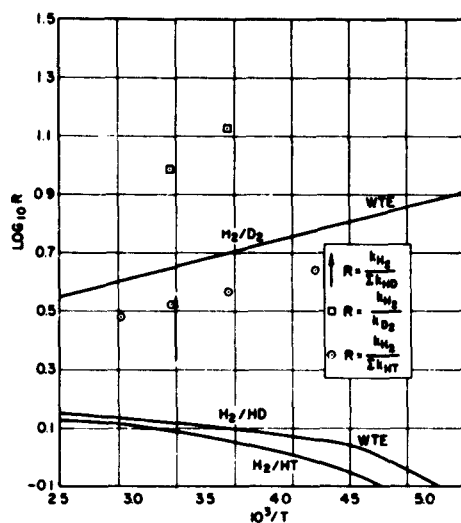


Figure 1. Relative reaction rates of isotopic hydrogen molecules with chlorine atoms as a function of temperature. Solid lines were calculated by Wheeler, Topley, and Eyring for the H_2Cl transition state.

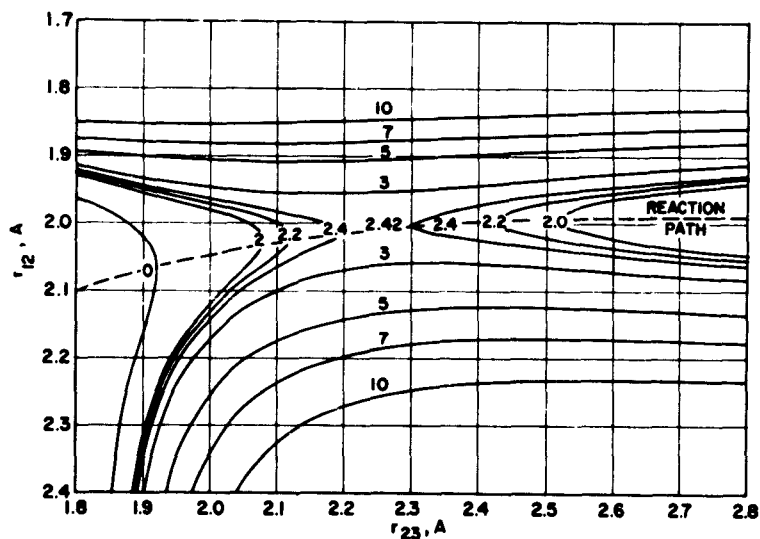


Figure 2. Potential energy surface for $\text{H} + \text{Cl}_2$ in vicinity of transition state using the Sato method of construction of surfaces, $K = 0$. (Contour lines are expressed in kcal/mole.)

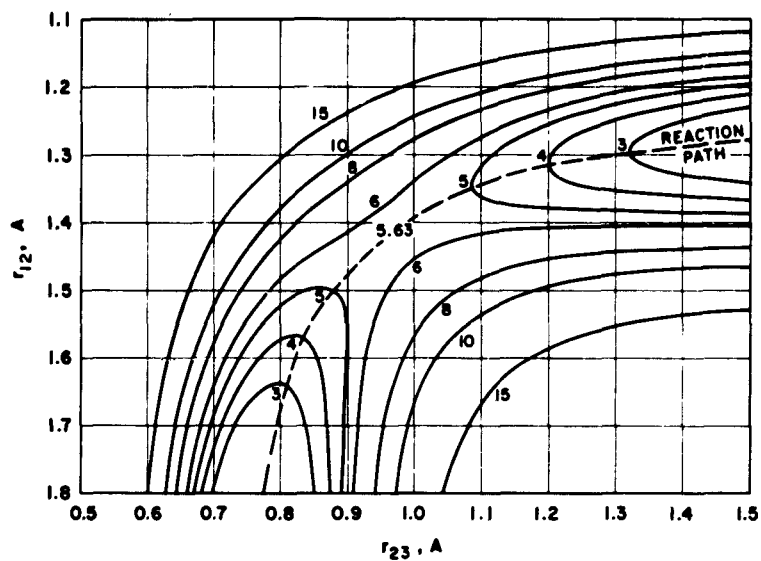


Figure 3. Potential energy surface for $\text{H} + \text{HCl}$ in vicinity of transition state using the Sato method of construction of surfaces, $K = 0.168$. (Contour lines in kcal/mole.)

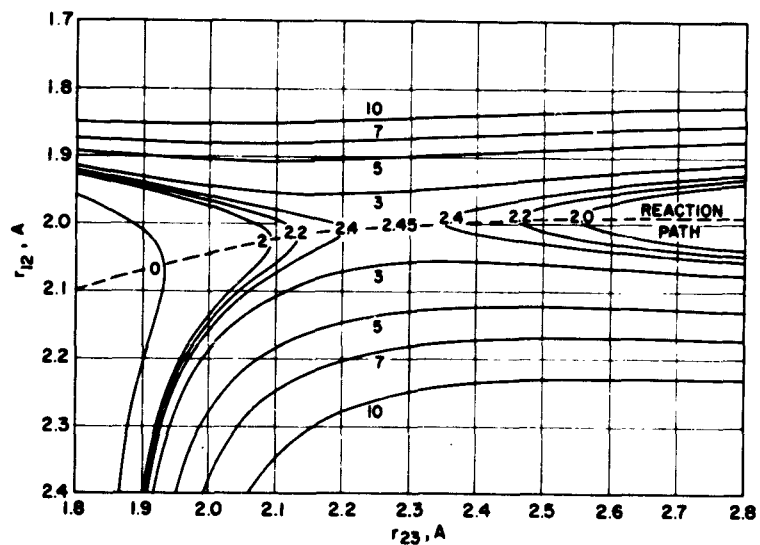


Figure 4. Potential energy surface for $\text{D} + \text{Cl}_2$ in vicinity of transition state using the Sato method of construction of surfaces, $K = 0$. (Contour lines in kcal/mole.)

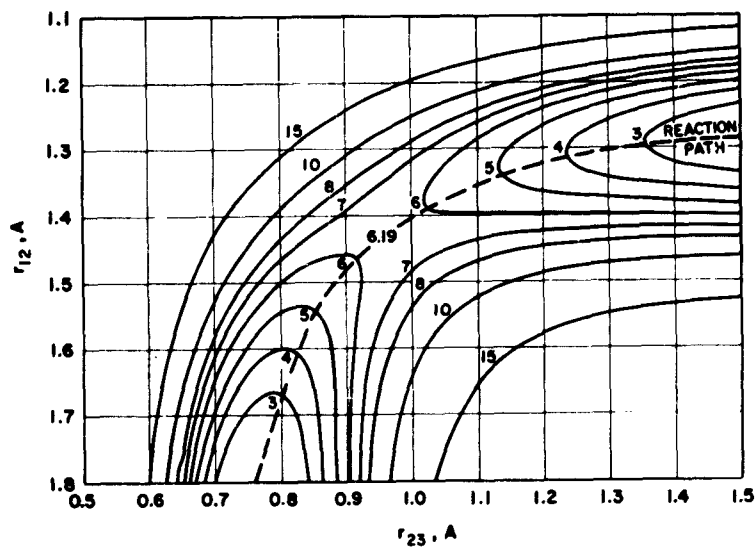


Figure 5. Potential energy surface for D + HCl in vicinity of transition state using the Sato method of construction of surfaces, $K = 0.168$. (Contour lines in kcal/mole.)

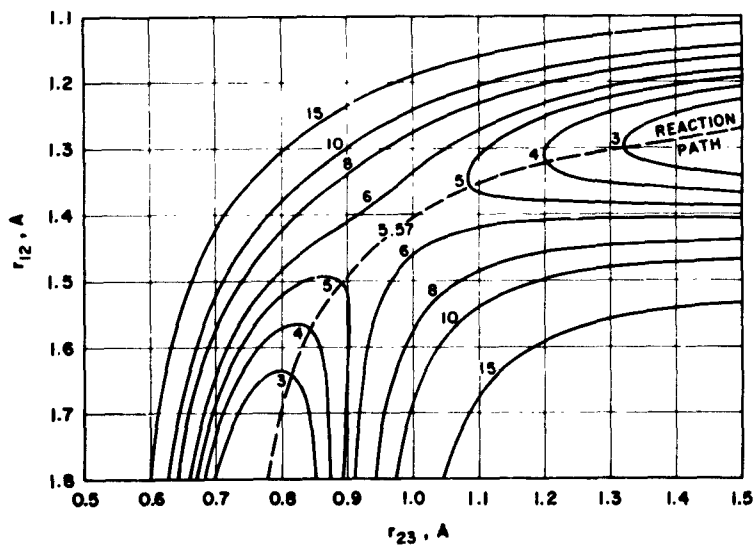


Figure 6. Potential energy surface for H + DCl in vicinity of transition state using the Sato method of construction of surfaces, $K = 0.168$. (Contour lines in kcal/mole.)

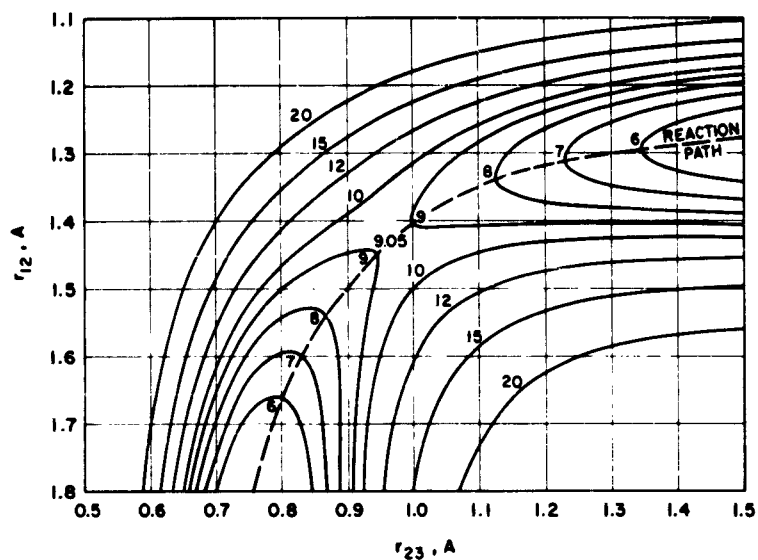
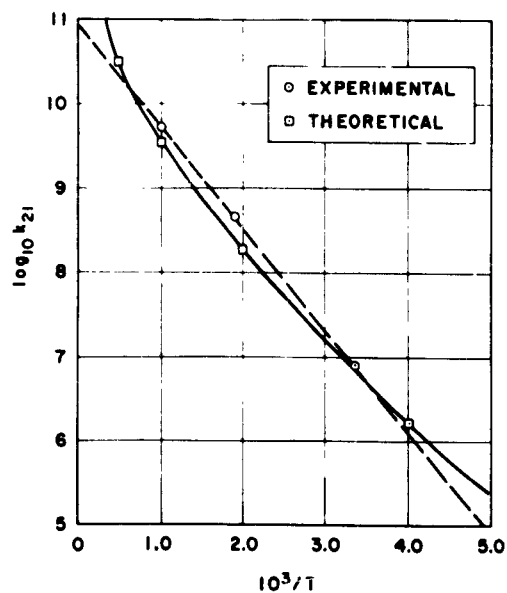


Figure 7. Potential energy surface for $D_2 + Cl$ in vicinity of transition state using the Sato method of construction of surfaces, $K = 0.168$. (Contour lines in kcal/mole.)

Figure 8. $\log_{10} k_{21}$ versus $10^3/T$ for reaction $H_2 + Cl$ going to $H + HCl$



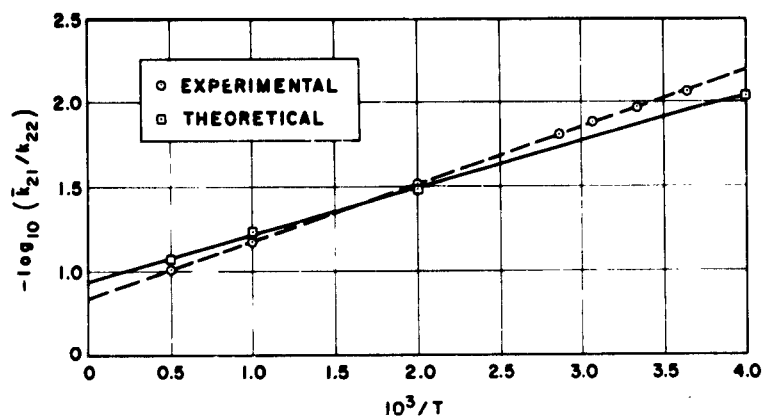


Figure 9. Relative rates of reaction of HCl and Cl₂ with chlorine atoms.

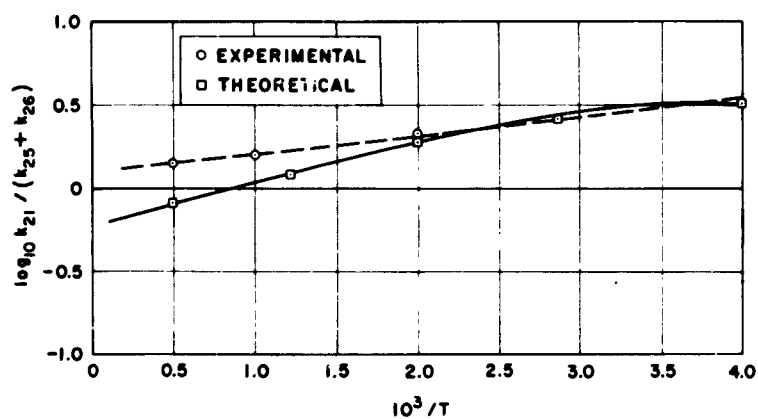


Figure 10. Relative rates of reaction of H₂ and HD with chlorine atoms.

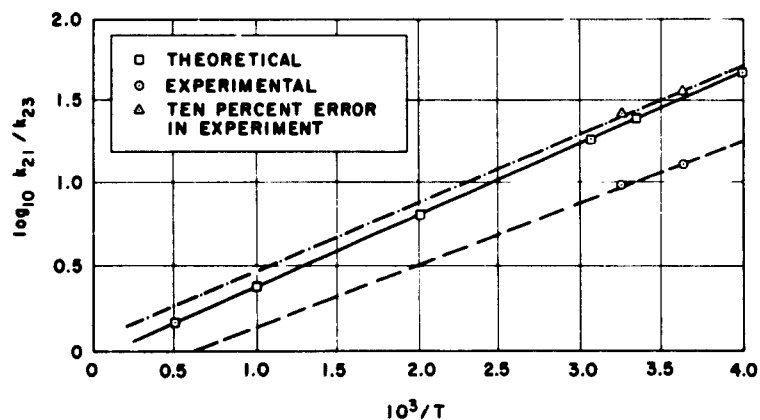


Figure 11. Relative rates of reaction of H₂ and D₂ with chlorine atoms.

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| <p>Aerospace Corporation, El Segundo, California. CALCULATION OF RATE COEFFICIENTS FOR SOME ELEMENTARY REACTIONS. I. HYDROGEN DEUTERIUM, DEUTERIUM HYDRIDE WITH CHLORINE, by Roger L. Wilkins. 15 May 1963. [28] p. incl. illus.</p> <p>(Report TDR-169(3230-10)TN-4; SSD-TDR-63-99) (Contract AF 04(695)-169) Unclassified report</p> <p>Rate coefficients are calculated for the reactions of hydrogen, deuterium, and deuterium hydride with chlorine. The potential energy surfaces of the isotopic transition complexes of HCl_2 and H_2Cl have been constructed by the Sato method to match experimental activation energies in accordance with absolute rate theory. The rate coefficients calculated using absolute rate theory are then used to evaluate the relative rates of reaction of H_2/HD, H_2/D_2 with chlorine atoms, and the relative rates of the fast reaction step (over)</p> | <p>UNCLASSIFIED</p> |
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| <p>H + Cl₂ compared to the back reaction H + HCl. The results agree very well with the few experimental values reported in the literature. Our theoretical calculations show that prior experimental values of the pre-exponential factors in the Arrhenius-type expression for rate constants are not required in order to obtain better information on the structure and vibrational frequencies of the transition states. The agreement of the activated complex theory with experiment was found to be satisfactory.</p> | <p>UNCLASSIFIED</p> |
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